

Chemical Analysis of Industrial Carbon Materials using Soft X-Ray Emission and Absorption Spectroscopy

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**Soft X-Ray Emission & Absorption Spectroscopy using
BL-6.0.1/6.0.2/8.0.1@ALS**

Light Element (B,C,N,O,Si) Materials

**Electronic-Structure/Chemical-Bonding Analysis
Industrial Application**

Why Carbon ?

Traditional & Frontier Materials

- | | |
|-----------------------|---|
| Fundamental materials | : carbon black, amorphous carbon, graphite, diamond fiber, alloy |
| Nano carbon | : fullerenes, nanotubes, nanodiamond |
| Electronic devices | : wide-gap semiconductor, superconducting material, magnetic material |
| Soft matter, | : bio-material |

Nice Target for X-Ray Emission Spectroscopy

Brilliant SR overcomes the low fluorescence yield

Surface (carbon) contamination can be negligible

Less sample damage in comparison with electron-beam-excitation methods

New analysis methods have been required in carbon industry

Recent Measurements@BL-8.0.1 in My Study

Industrial Applications

- (1) Electronic structure analysis of **wide-gap semiconductors; B-doped diamond**
- (2) Spectral data base; **Polycyclic aromatic hydrocarbon (PAH)**
- (3) Microstructure/chemical analysis of **carbon films on Japanese smoked roof tile**
- (4) Electronic structure analysis of BCN composites
- (5) Characterization of C-doped Metals

Spectroscopy/New Technique

- (1) Angle-dependent resonant inelastic x-ray scattering of oriented materials
- (2) X-ray emission measurements under the x-ray standing-wave conditions
for non-destructive chemical analysis of interface of multilayer mirrors

Electronic Structure Analysis of B-Doped Diamond

J.Iihara, Y. Muramatsu et al., J.Appl.Phys.(to be published)

B-doped Diamond

Wide-gap semiconductor
Superconducting!(E.A.
Ekimov,Nature,428,542 (2004))

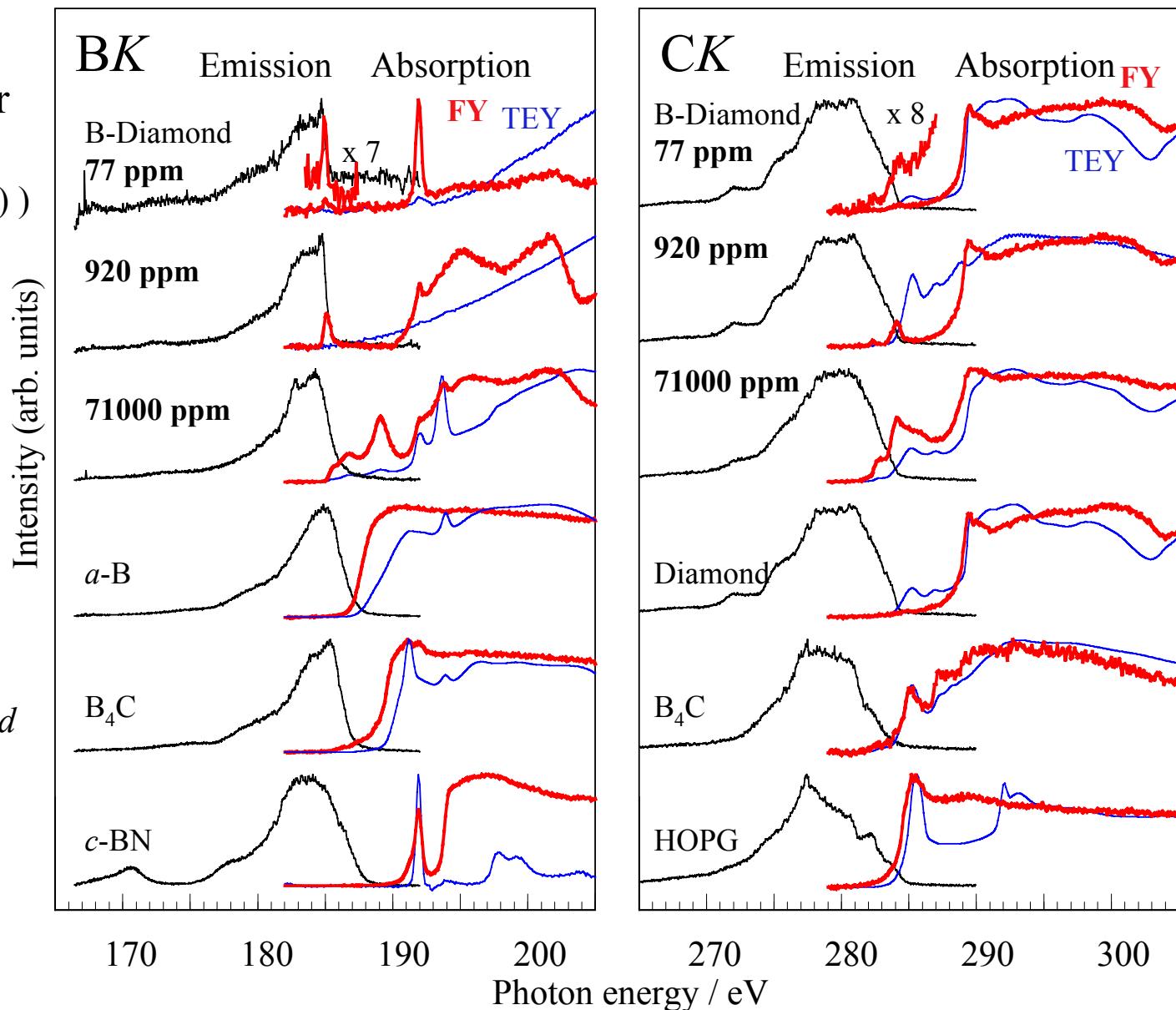


Evaluation and control of band-gap

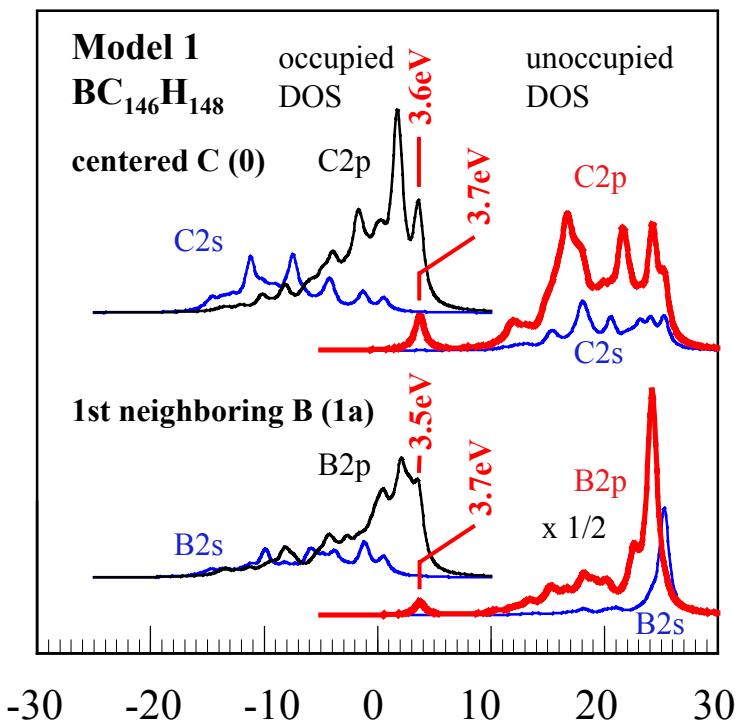
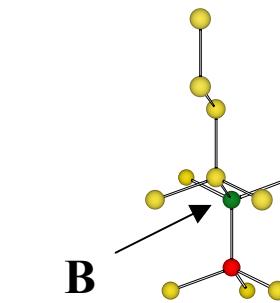
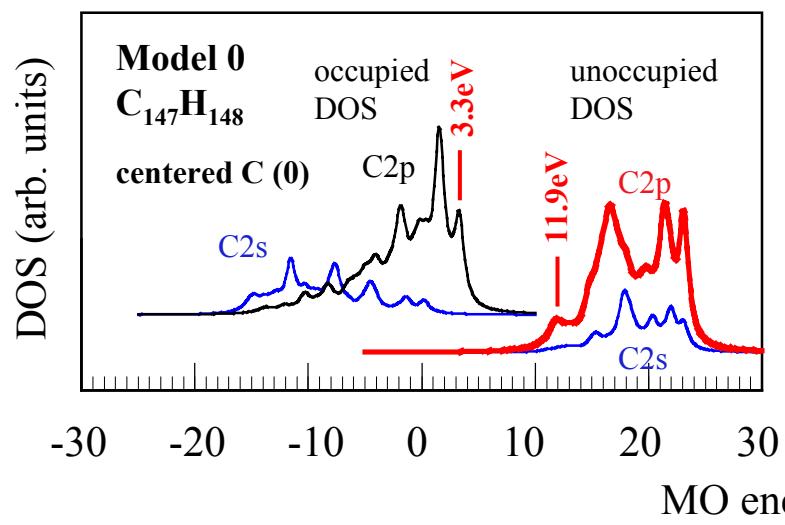
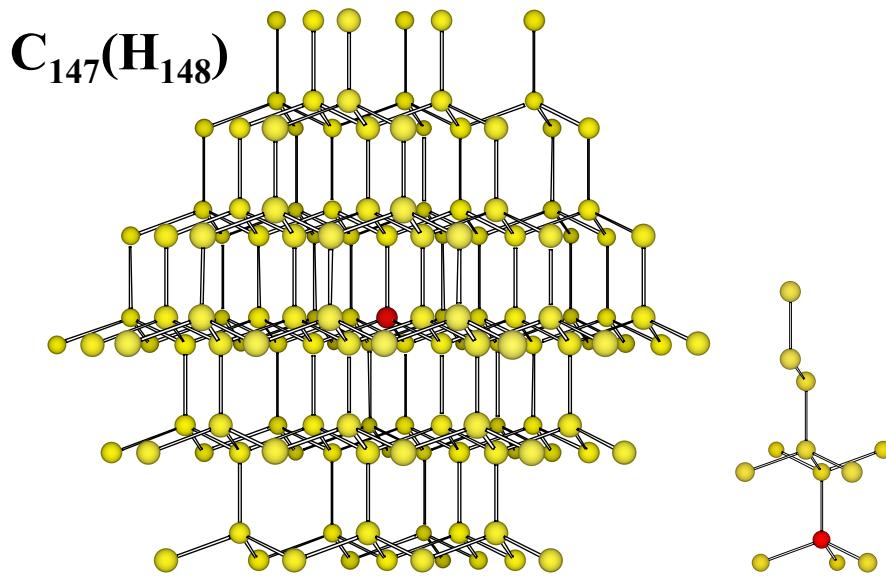
Pioneering measurements
(J.Nakamura et al. PRB
(accepted))

B-doped diamond preparation
Sumitomo Electric Industries, Ltd

B-conc./ppm	R/Ωcm
77	23
920	0.1
71000	0.03

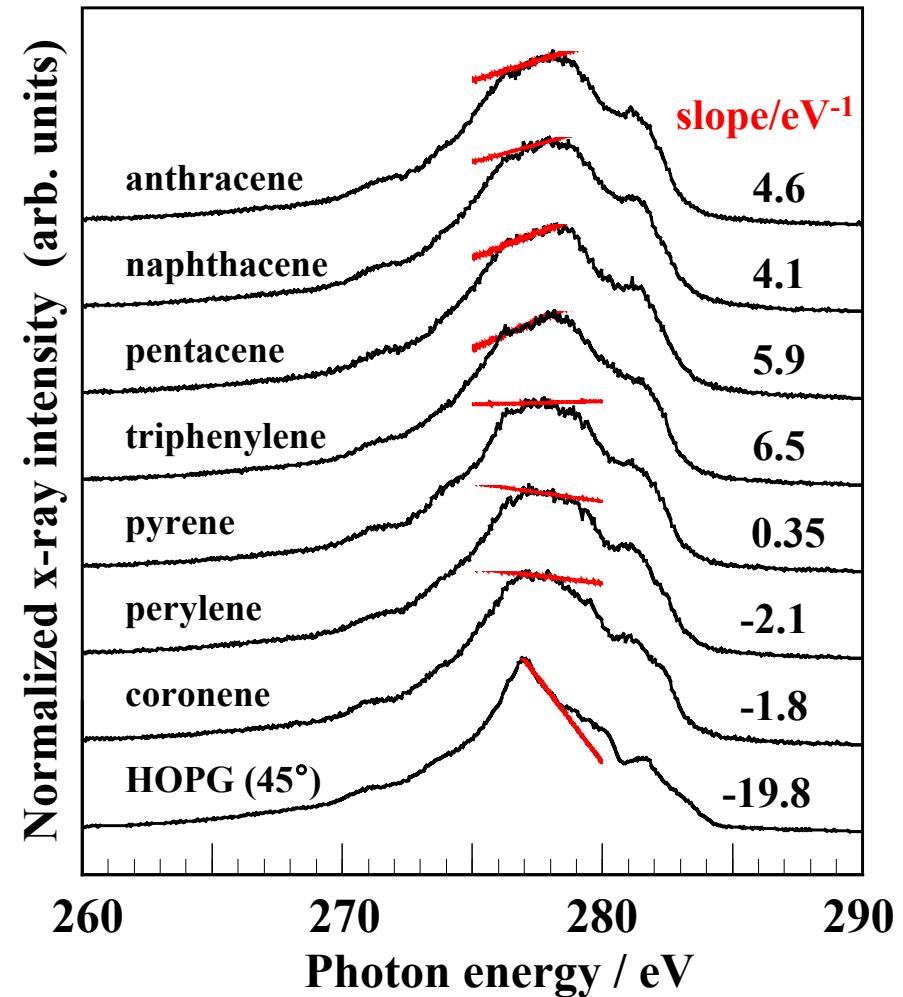
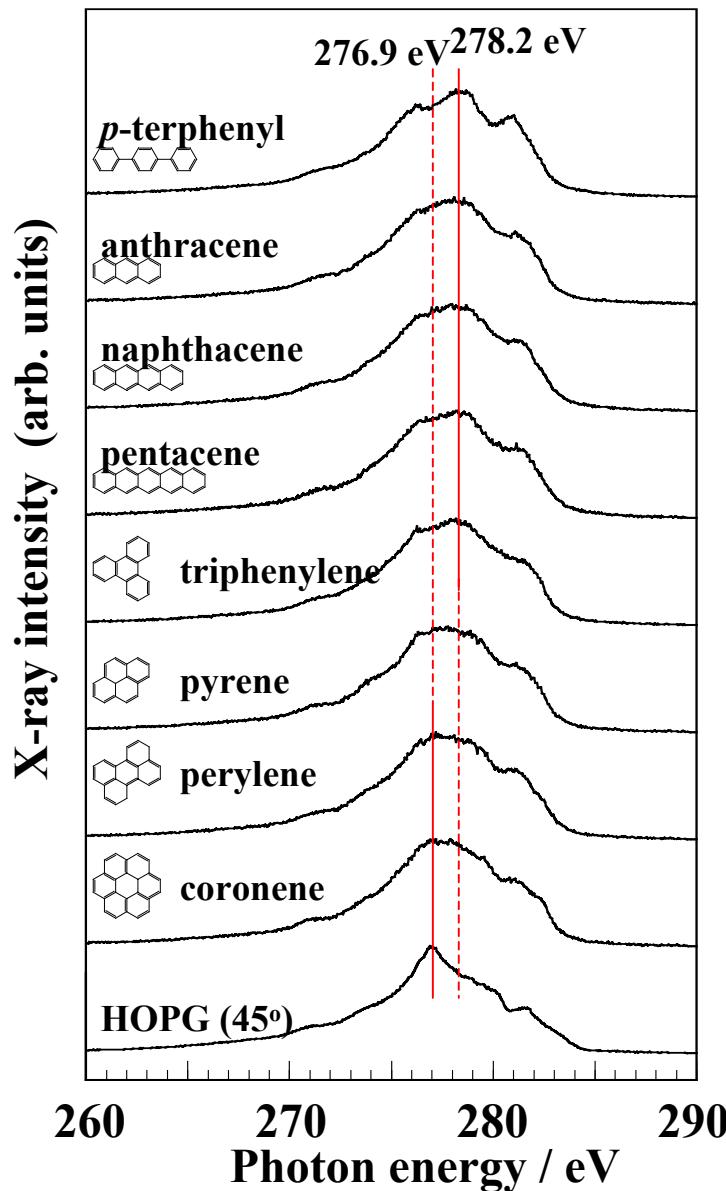


Electronic Structure Calculations using DV-X α MO Methods



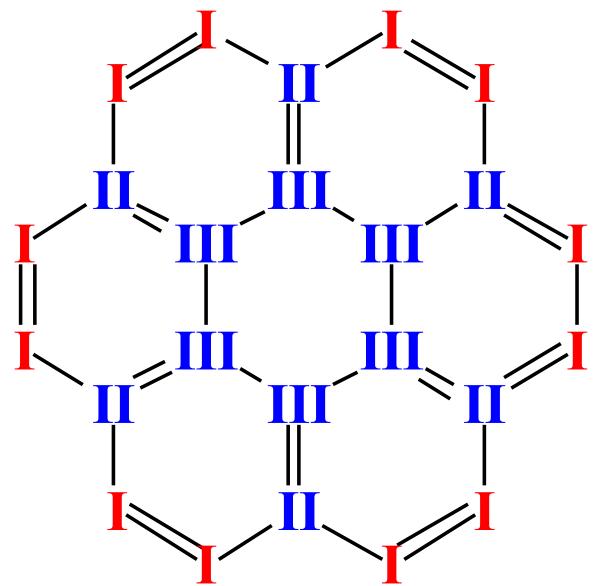
X-Ray Emission Spectroscopy of PAH

Y.Muramatsu et al., J.Electron Spectrosc.Relat.Phenom., 137-140, 823-826(2004)

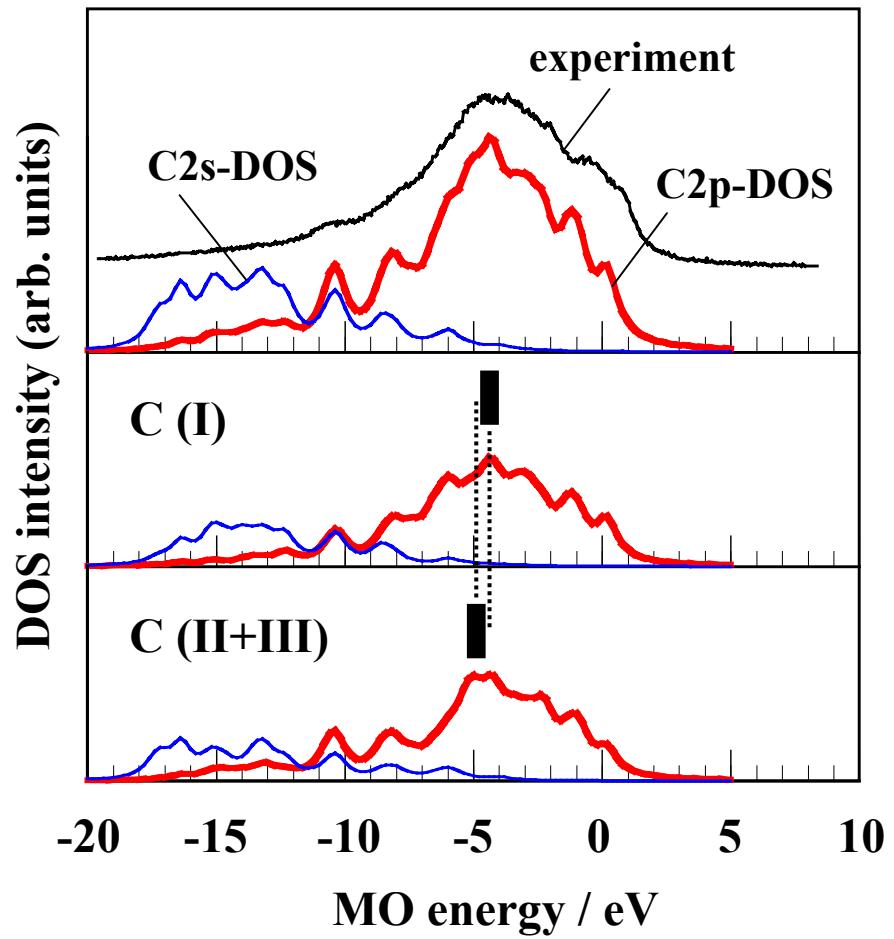


Spectral Analysis of Coronene by DV-X α Methods

Molecular structure of coronene

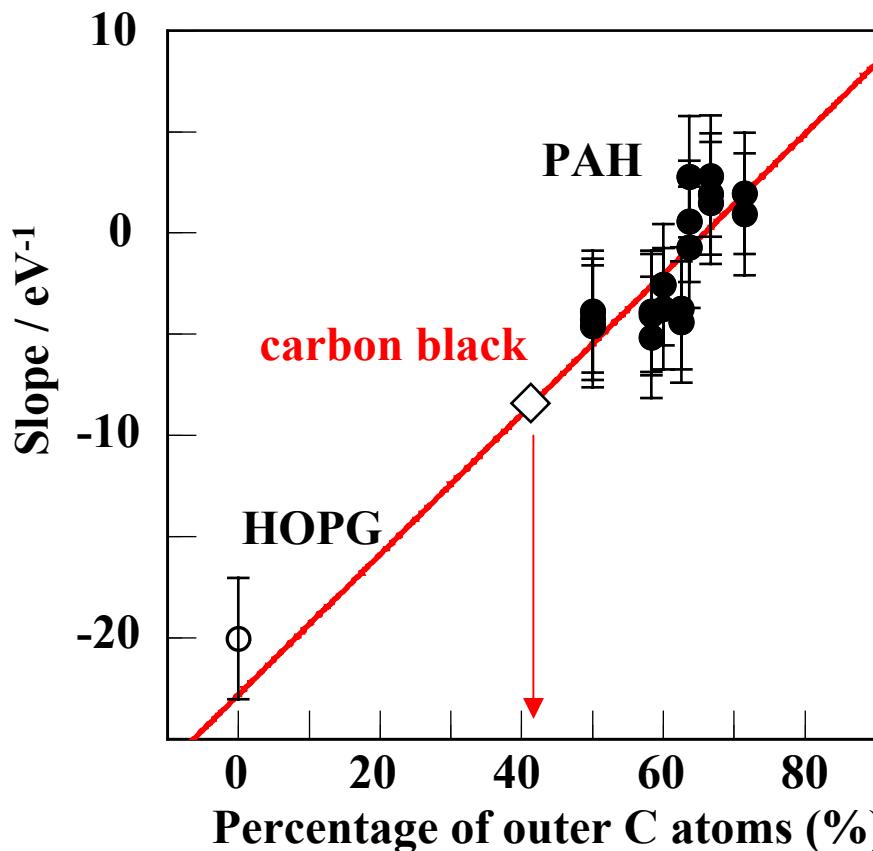


Calculated DOS spectra of coronene

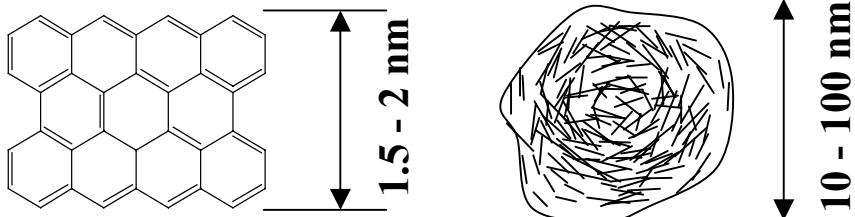


Structural Information from the X-Ray Emission Spectra?

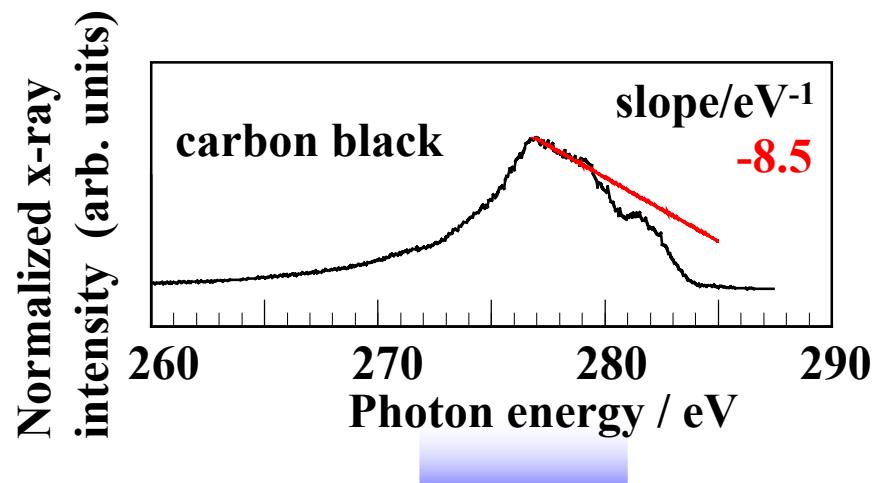
Approximated slopes near the main peaks of several PAH compounds



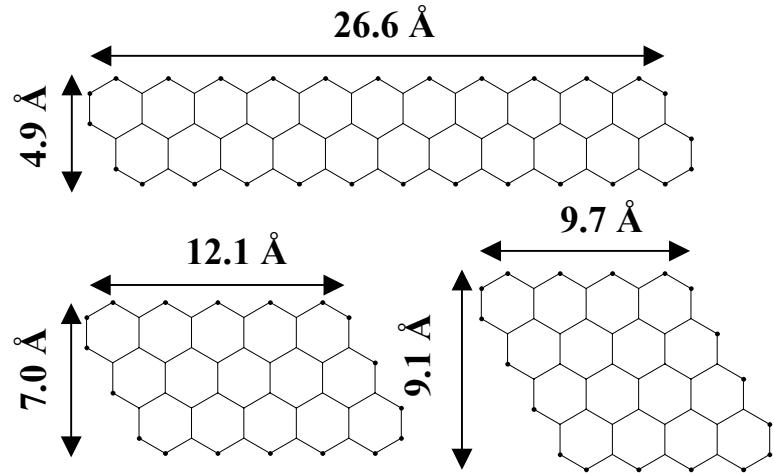
Particle models of carbon black



CK x-ray emission spectra of carbon black



Estimated PAH structures of carbon black

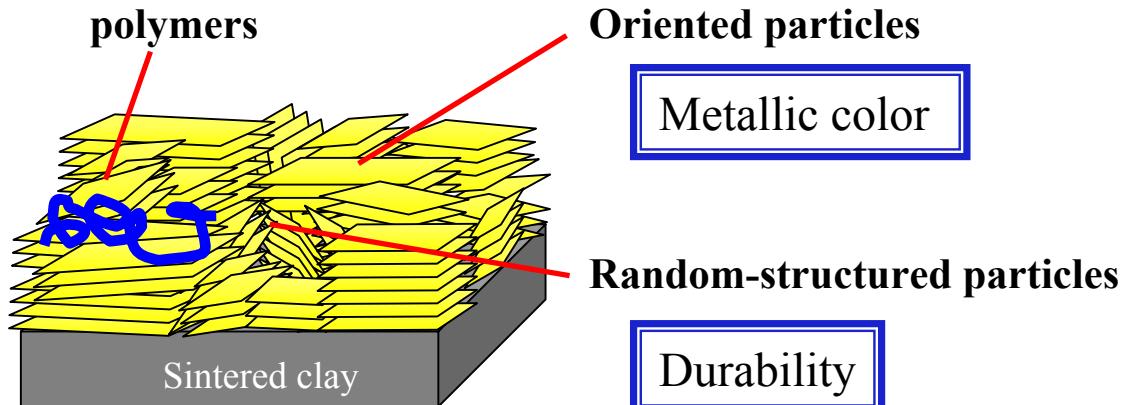
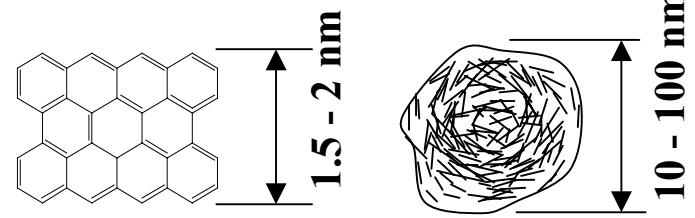
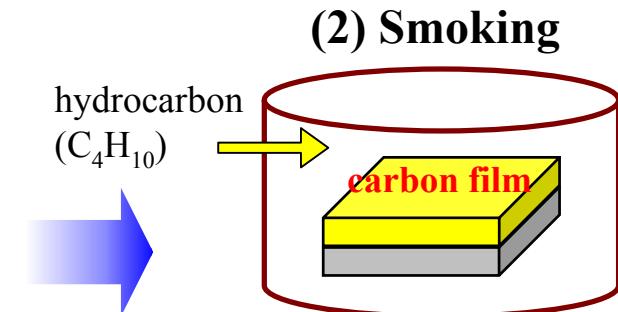
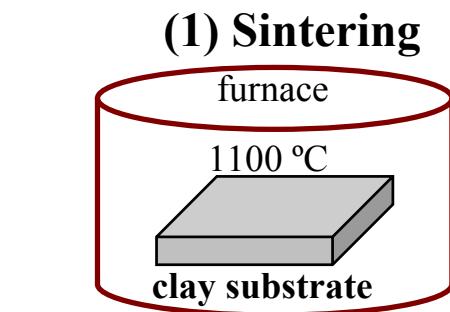
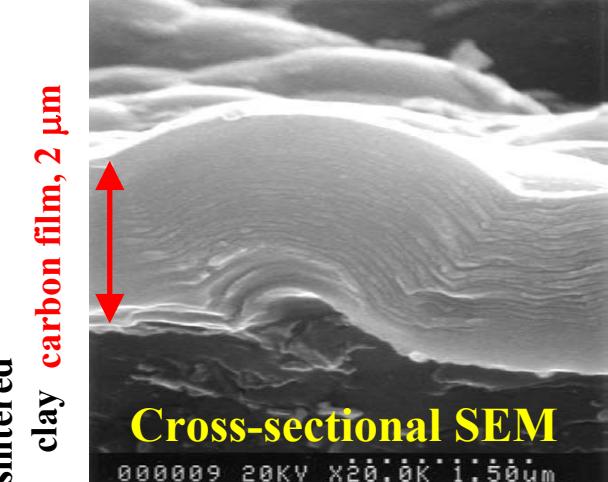
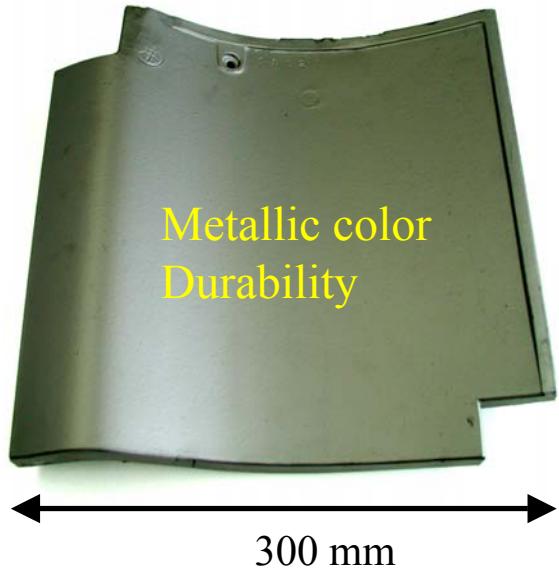


Carbon Films on Japanese Smoked Roof Tiles

Y. Muramatsu et al., *Jpn. J. Appl. Phys.*, 42, 6551-6555 (2003)

Y. Muramatsu et al., *Spectrochimica Acta B*, 59, 1317-1322 (2004)

Smoked roof tile, "Kawara"



Weathering Effect on Kawara

Weathered Kawara



Kawara-1994
(weathered for 8 years)



Kawara-1997
(5 years)



Kawara-1999
(3 years)



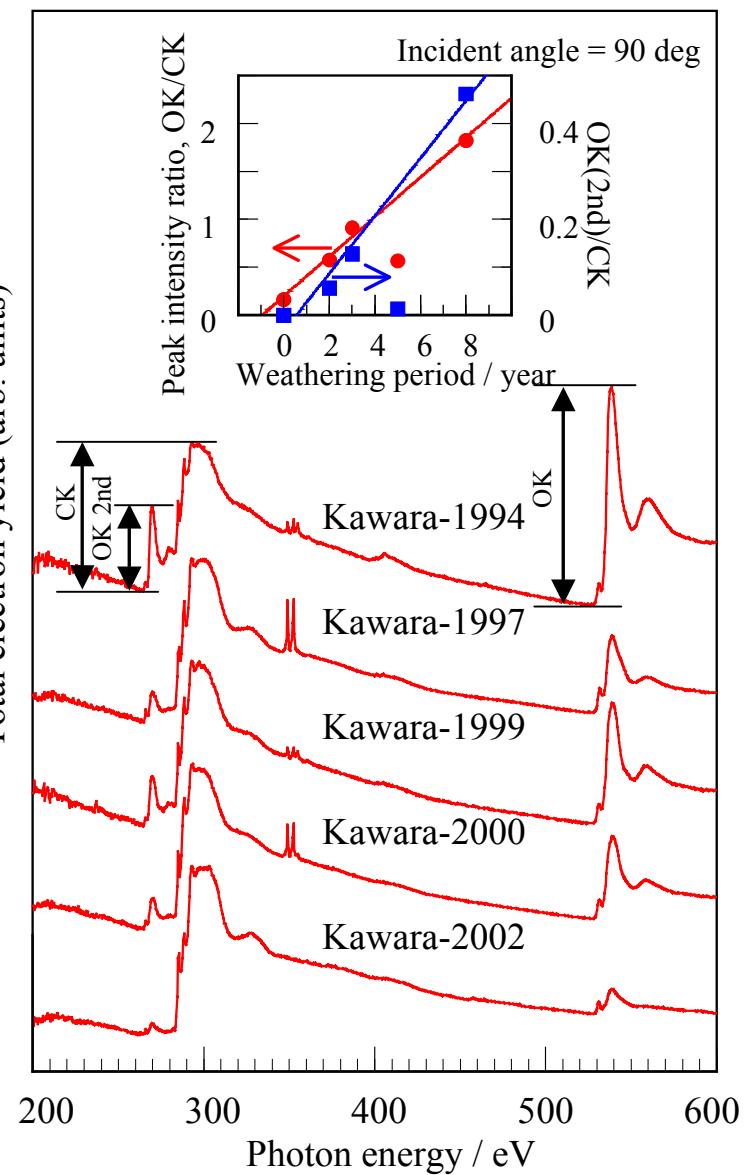
Kawara-2000
(2 years)



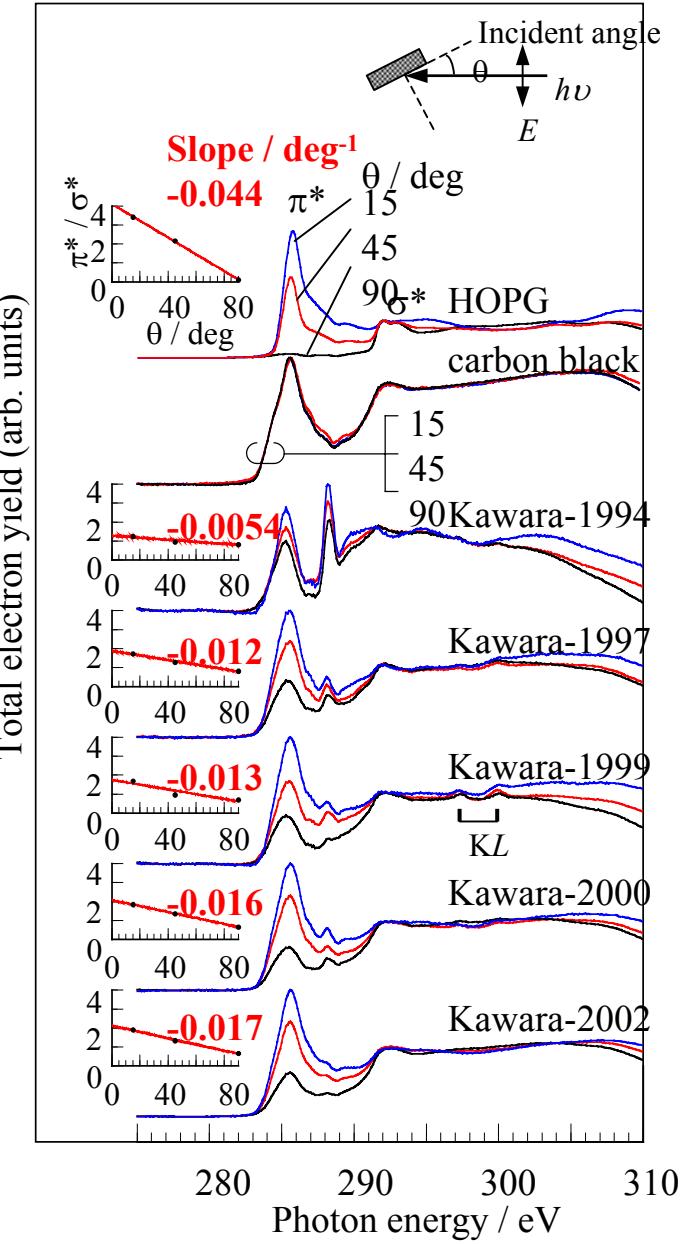
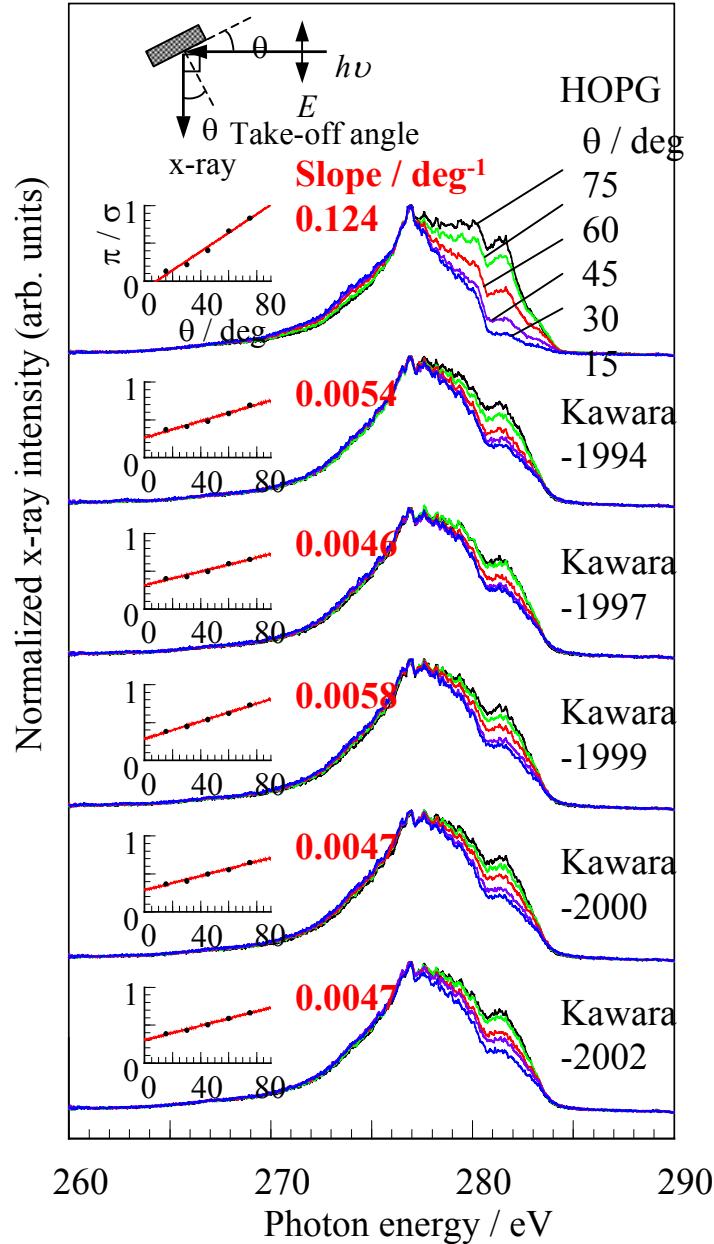
Kawara-2002
(0 year)

↔
10 mm

TEY X-ray absorption spectra



Angle-dependent X-Ray Emission and TEY Absorption Spectra

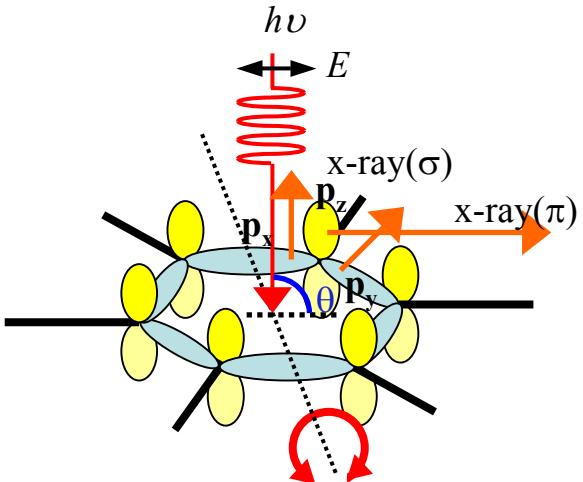


Anisotropy of X-Ray emission and Absorption in Graphite

Emission

$$I_{\text{emi}}(E, \theta) = I_{\sigma \text{ emi}}(E) \{(1 + \cos^2\theta)/2\} + I_{\pi \text{ emi}}(E)\sin^2\theta$$

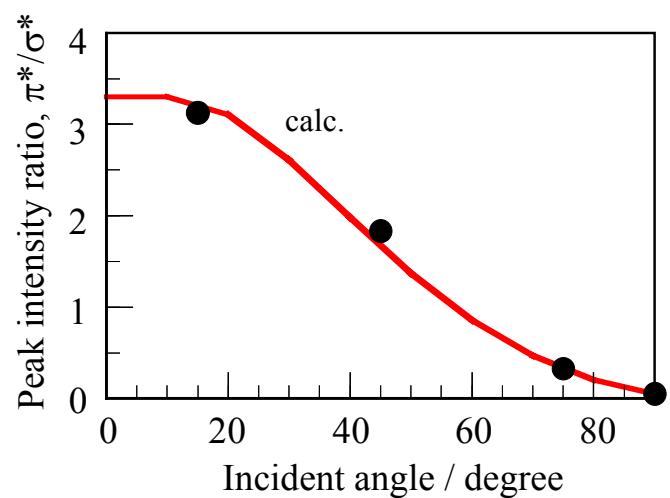
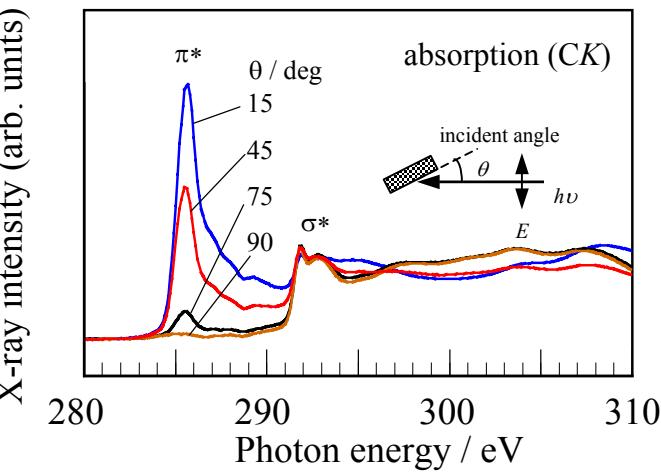
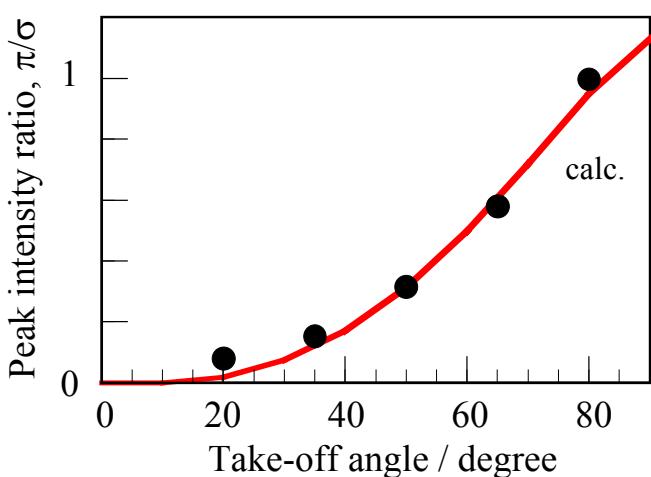
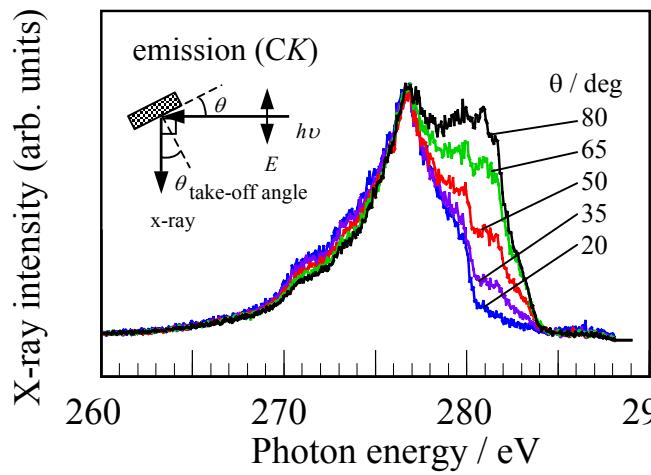
$$I_{\pi \text{ emi}}(E)/I_{\sigma \text{ emi}}(E) = K \sin^2\theta/(1 + \cos^2\theta) \quad (\text{K: constant})$$



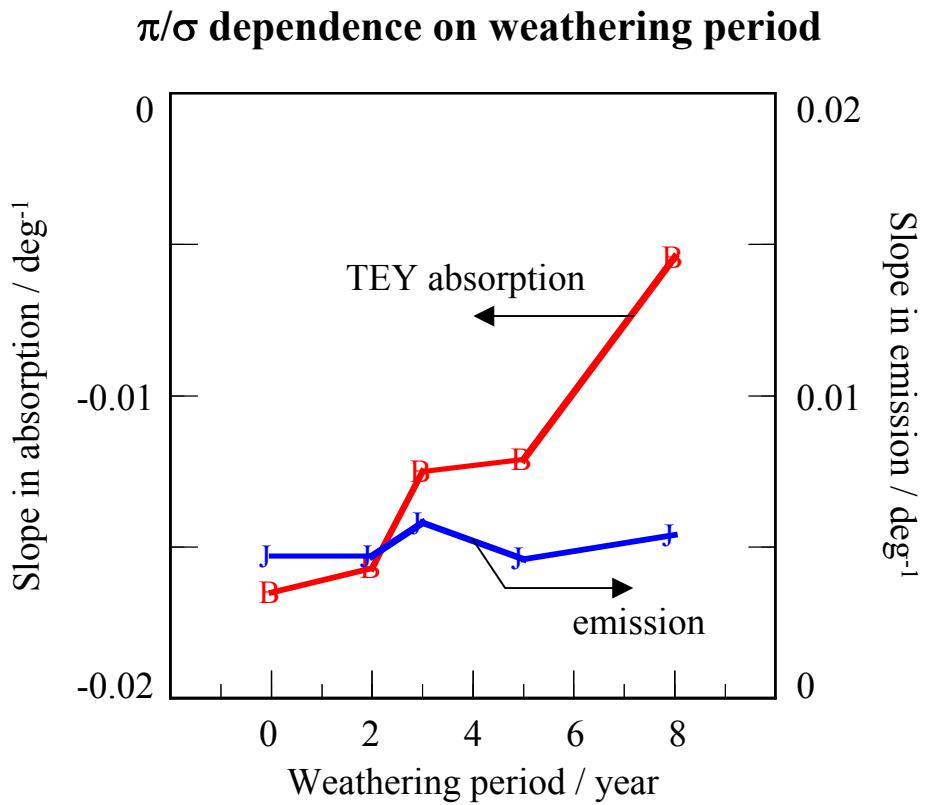
Absorption

$$I_{\text{abs}}(E, \theta) = I_{\sigma \text{ abs}}(E) \{(1 + \sin^2(\theta))/2\} + I_{\pi \text{ abs}}(E)\cos^2(\theta)$$

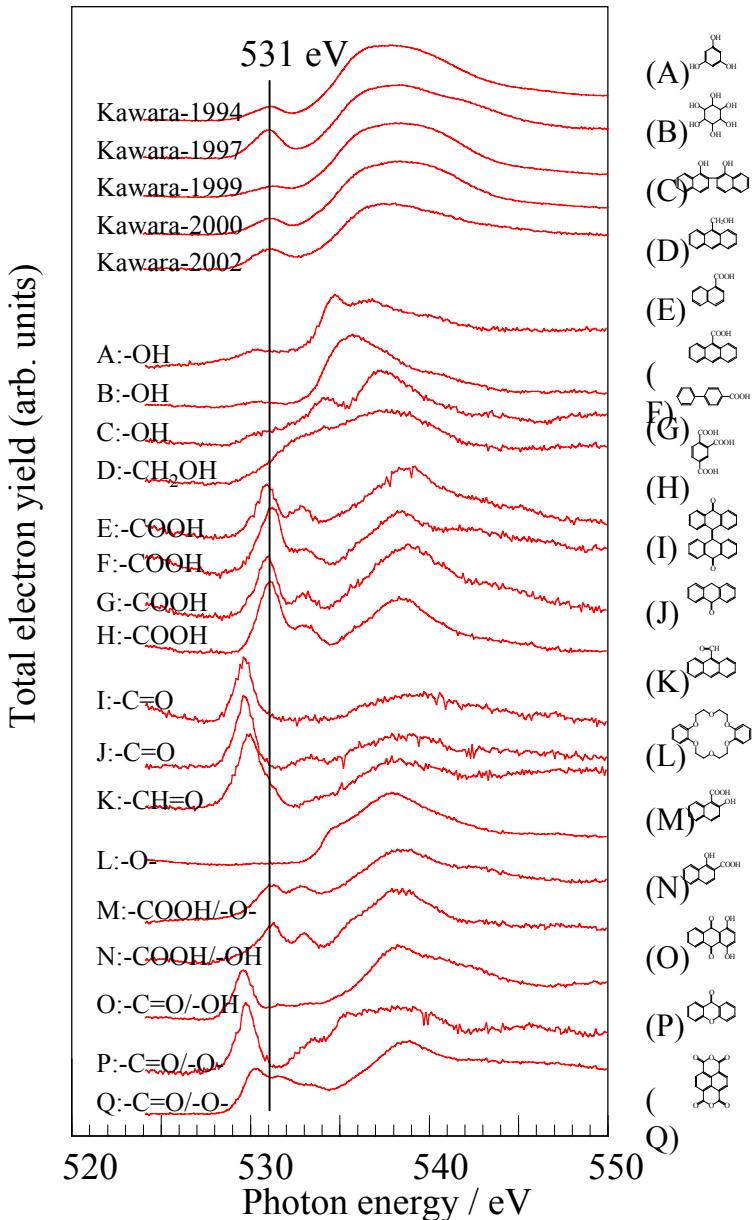
$$I_{\pi \text{ abs}}(E)/I_{\sigma \text{ abs}}(E) = K \cos^2\theta/(1 + \sin^2\theta) \quad (\text{K: constant})$$



Oxidation of the Surface Carbon Films on Kawara



- Weathering degrades and oxidizes the surface carbon films, which causes the metallic silver color to change into darker gray. Orientation of inner carbon films have been kept for 8-year weathering.
- The oxidation state is mainly $-\text{COOH}$.



Conclusion

X-ray emission spectroscopy is powerful tool for electronic-structure/chemical-bonding analysis of industrial carbon materials.

Special thanks to

Dr. J. D. Denlinger, Dr. E. M. Gullikson, and Dr. R. C. C. Perera